

O

AR-009-374  
DSTO-TR-0237

T

Hydrocarbon Adsorbents:  
A Potential Polishing Step to Treat  
Shipboard Oily-water Waste

Lyn E. Fletcher and F.J. Upsher

S

19960429 023

APPROVED FOR PUBLIC RELEASE

© Commonwealth of Australia

DTIC QUALITY INSPECTED 1

D

DEPARTMENT OF DEFENCE  
DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION

# Hydrocarbon Adsorbents: A Potential Polishing Step to Treat Shipboard Oily-Water Wastes

*Lyn E. Fletcher and F. John Upsher*

**Ship Structures and Materials Division  
Aeronautical and Maritime Research Laboratory**

DSTO-TR-0237

## ABSTRACT

Current shipboard oily-water waste (OWW) separators installed on RAN ships frequently fail to reduce oil concentrations in OWW to specified discharge limits. The presence of detergents is the major interference. This report examines the potential of hydrocarbon adsorbents to polish OWW containing detergents, to meet the 15 mg/l MARPOL discharge limit. Test OWWs were prepared containing a variety of detergents and tested with a hydrocarbon adsorbent. Results showed that strongly emulsifying detergents affected effluent quality, though some oil reduction in the effluent was experienced. Other less strongly emulsifying detergents, particularly fast breaking detergents, had little effect on oil and grease concentrations in the effluent. When these detergents were present in OWW, oil and grease concentrations could be reduced to less than 15 mg/l. Flow rates and adsorbent housing design also affected effluent quality when strongly emulsifying detergents were present. Consequently, hydrocarbon adsorbents could be used to reduce oil concentrations to the lower MARPOL discharge limit of 15 mg/l, provided some restrictions are also placed on shipboard detergent use, and adsorbent housings are constructed to minimise internal turbulence.

## RELEASE LIMITATION

*Approved for public release*

DEPARTMENT OF DEFENCE

DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION

*Published by*

*DSTO Aeronautical and Maritime Research Laboratory  
PO Box 4331  
Melbourne Victoria 3001*

*Telephone: (03) 9626 8111  
Fax: (03) 9626 8999  
© Commonwealth of Australia 1996  
AR No. 009-374  
January 1996*

**APPROVED FOR PUBLIC RELEASE**

# Hydrocarbon Adsorbents: A Potential Polishing Step to Treat Shipboard Oily-Water Wastes

## Executive Summary

Discharge of oily-water wastes (OWW) from ships contributes as much oil into the marine environment as tanker accidents. Consequently, there is major international effort to control such discharges. The International Maritime Organisation regulates OWW discharges through MARPOL 73/78. This limits the amount of oil and grease that can be discharged from a moving ship to less than 15 mg/l when within 12 nm from land, to below 100 mg/l when beyond 12 nm and prohibits discharge in the Great Barrier Reef Marine Park.

Royal Australian Navy (RAN) ships are currently fitted with a variety of OWW separators intended to reduce oil in OWW to either below 15 mg/l or 100 mg/l. In practice, these separators frequently fail to achieve this because of the presence of detergents. Consequently, there is a need to identify a technique capable of reducing oil and grease concentrations in the presence of detergents. This report examines the potential of hydrocarbon adsorbents to polish OWW after treatment by existing shipboard OWW separating equipment, to produce an effluent with an oil concentration of less than 15 mg/l.

A hydrocarbon adsorbent from Environ-smart was used for testing. This adsorbent is a mixture of activated carbon and a polymeric adsorbent used in oil booms. Test OWW was prepared to simulate emulsified OWW after passage through an OWW separator rated to 100 mg/l. Test OWW contained tap water, seawater, an oil and grease mixture and test detergents. Two rigs were trialed to assess the effects that design parameters have on adsorbent performance. The effect of flow rate was also considered. The efficiency of the process was determined by measuring the oil and grease concentration in the test OWW before and after treatment by the adsorption units.

The type of detergent present in OWW had a large effect on adsorbent performance. This was found to depend on the ability of the detergent to form stable surfactant emulsions called micelles. Only when fast breaking detergents which do not form micelles, or when detergents which form only partial micelles were present could an effluent containing less than 15 mg/l be produced. Strongly emulsifying detergents like Gamosol, a detergent used frequently to clean engine rooms and machinery spaces on RAN ships, interfered substantially with the adsorption process. Flow rates and unit design also affected performance and their effect was more enhanced when strongly emulsifying detergents were present.

This work has shown that hydrocarbon adsorbents could be used in a polishing step to improve OWW effluent quality. A hydrocarbon adsorption unit could be added to existing OWW separators rated to 100 mg/l, to convert them to units capable of reducing oil and grease concentration to less than 15 mg/l. However, for this to be successful some further control on detergent use on board RAN ships is required. Fast breaking detergents could be used instead of emulsifying detergents during the cleaning of engine rooms and auxiliary machine rooms which would also put less load on current separators. Exhausted hydrocarbon adsorbents could be simply replaced and stored on board for disposal at shore, requiring minimal maintenance and storage.

## Authors

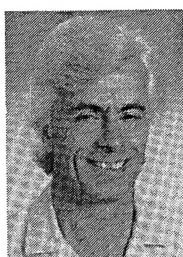


**Lyn E. Fletcher**

Ship Structures and Materials Division

*Lyn Fletcher, BAppSc (Chem.) (RMIT) joined Aeronautical and Maritime Research Laboratory in 1985 and worked for three years on research into polymer and solvent interactions. She then joined a small multidisciplinary group investigating some environmental problems encountered by the Royal Australian Navy. In support of this work, Lyn is currently studying for a MEnvSc at Monash University.*

---



**F. John Upsher**

Ship Structures and Materials Division

*John Upsher, BSc Hons (Bath), MSc (La Trobe), joined Aeronautical and Maritime Research Laboratory as a microbiologist in 1966 then for 20 years investigated different problems associated with microbial deterioration of materials and equipment in storage and in the tropical environment. Responding to increasing concern within Defence on environmental matters, he has more recently investigated the bacterial generation of hydrogen sulfide in naval oily water wastes and the disposal of wastes including sewage and plastics.*

---

# Contents

|  |    |
|--|----|
| 1. INTRODUCTION .....  | 1  |
| 2. MATERIALS AND METHODS .....                                   | 2  |
| 2.1 Reagents .....   | 2  |
| 2.2 Preparation of Test OWW .....                                | 2  |
| 2.3 Configuration of Environ-smart Oil Filter Prototype #1 ..... | 2  |
| 2.4 Configuration of Environ-smart Oil Filter Prototype #2 ..... | 3  |
| 2.5 Analytical Methods .....                                     | 4  |
| 3. RESULTS AND DISCUSSION .....                                  | 4  |
| 3.1 Effect of Test OWW Composition on Effluent Quality .....     | 4  |
| 3.2 Effect of Flowrate on Effluent Quality .....                 | 7  |
| 3.3 Effect of Adsorbent Unit Design .....                        | 8  |
| 4. CONCLUSION .....  | 10 |
| 5. ACKNOWLEDGEMENTS .....  | 10 |
| 6. REFERENCES .....  | 10 |

## 1. Introduction

Oil is a significant marine environmental pollutant. The amount of oil released into the marine environment has been estimated to be around 3.2 million tons annually of which 1.5 million tons is thought to originate from transportation (Doerffer, 1992). The contribution from discharging bilge and other oily-water wastes from shipping is thought to range between 0.2 to 0.6 million tons annually which is comparable to the contribution from tanker accidents, 0.3 to 0.4 million tons annually (Doerffer, 1992). Consequently, significant international effort is being made to control this discharge.

The International Maritime Organisation (IMO) regulates this discharge through the International Convention for the Prevention of Pollution from Ships, commonly known as MARPOL 73/78. This prescribes the amount of oil and grease that can be discharged to below 15 mg/l when the ship is within 12 nm of land, within 12 nm of the outer edge of the Great Barrier Reef, or in a designated special area, to below 100 mg/l when the ship is greater than 12 nm from land, and prohibits discharge in the Great Barrier Reef Marine Park (IMO, 1992).

The Royal Australian Navy (RAN) fleet is diverse and consequently contains a variety of equipment. The RAN is currently involved in a program to up-date pollution control equipment in ships to meet the more stringent requirement of less than 15 mg/l. Most ships are fitted with plate coalescing or centrifugal separators rated to remove oil and grease to below 100 mg/l, although some larger supply ships have separators rated to less than 15 mg/l. These separators all frequently fail to meet the required effluent quality, and large quantities of oily-water wastes (OWW) have to be stored. Storage space for OWW can easily be exceeded which can restrict ships' movements. Moreover, prolonged storage of OWW can cause occupational health and safety problems through the production of toxic hydrogen sulfide gas which has resulted in fatalities in one RAN ship (Hodgeman, *et al.* 1995).

This problem of traditional separators failing to meet specification is not restricted to the RAN (Haupt, 1989; Smookler & Alig, 1992). One UK study of merchant ships with separators rated to less than 15 mg/l, found 60% of separators were failing to produce an effluent of less than 15 mg/l. Ranges observed were 1 to 110 mg/l (Anon, 1995). In addition, individual countries and states have the right to further legislate. Florida, for example, has mandated a 5 mg/l standard which has caused problems for one US Naval ship (Guida, 1994).

The major factor hindering the efficient separation of oils in these traditional technologies is the presence of stable emulsions caused by detergents and other emulsifying chemicals contained in some lubricating oils. Consequently, there is a need for new techniques that can be used alone or in conjunction with existing separators to consistently reduce oil concentrations in wastes containing emulsifiers. For naval vessels there is the additional requirement that any pollution control device should be small and easy to install without a major re-fit being required.



One technique that is being considered for RAN ships is the adoption of an adsorption unit to polish the OWW after the bulk separation of oil and water has been performed in the present separators. This technique has the advantage of being simple to attach to existing equipment, and it should require minimal maintenance. New commercial mixed adsorbents based on a mixture of activated carbon and an oil absorbing polymer, similar to polymeric adsorbents used in oil booms are now available. This study investigates the performance of one such adsorbent in the presence of detergents and its potential for adoption on naval vessels.

## 2. Materials and Methods

### 2.1 Reagents

The oils were supplied by Fuels and Lubricants Section, AMRL, and consisted of F 76 diesel fuel (density of 0.846 kg/l), OMD 113 oil and a drive shaft coupling grease (Syntek Pty Ltd). The detergent Gamosol was acquired from Gamlen Australasia, Lane Cove, NSW, Comprox was acquired from BP Australasia, Melbourne, Vic. and Vecom was acquired from Port Marine Services, Port Melbourne, Vic. All other chemicals used were of reagent grade quality or better. The adsorbent was obtained from Environ-smart, Melbourne and was composed of activated carbon and a styrenated diene copolymer.

### 2.2 Preparation of Test OWW

A stock oil mix which consisted of 50%w/w diesel fuel, 49% OMD 113 oil and 1% grease was mixed in a high speed stirrer until the grease was completely suspended in the oils. Test OWW were then prepared by adding 63 litres of tap water to a storage tank, and emulsifying the required amount of the oil mix and detergents in 7 litres of seawater. This was done in stages using a Waring industrial blender. For experiments using mixtures containing 1000 ppm of oil, it was also necessary to blend the oil mix with tap water. The test emulsified OWW was used immediately.

### 2.3 Configuration of Environ-smart Oil Filter Prototype #1

Prototype #1 (Figure 1) consisted of two 20 l metal containers filled with adsorbent. Input was to the top of the first can and the outlet from this can was located 2/3rds from the bottom of the can, which fed into the top of the second. The outlet from the second can was again 2/3rds from the bottom of the can. Test OWWs were pumped through coarse filters to remove particulates before being fed into the filters. The flow was adjusted by means of a clamp attached to the inlet hose. To ensure a steady state,

sixty litres of test OWW was pumped through the unit before final samples were taken for analysis.

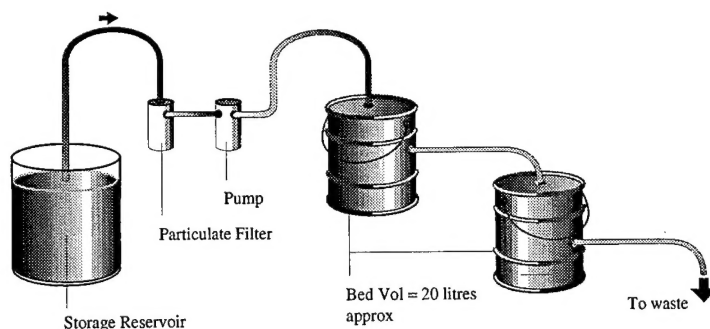


Figure 1: Schematic Diagram of Environ-smart Unit - Prototype #1

## 2.4 Configuration of Environ-smart Oil Filter Prototype #2

Prototype #2 (Figure 2) consisted of a series of 160 mm ID PVC tubes filled with the absorbent. These could be arranged to have the inlet at the top of the units with the outlet at the bottom or vice versa. Set-up #1 had the inlet at the bottom of the tubes while for set-up #2 the inlet was at the top. The OWWs were sampled at three points: the first prior to the unit, the second after the unit, and the third (an intermediate sample) between the large initial tube and the first of the three smaller tubes. No samples were taken until at least 60 litres of test OWW was treated.

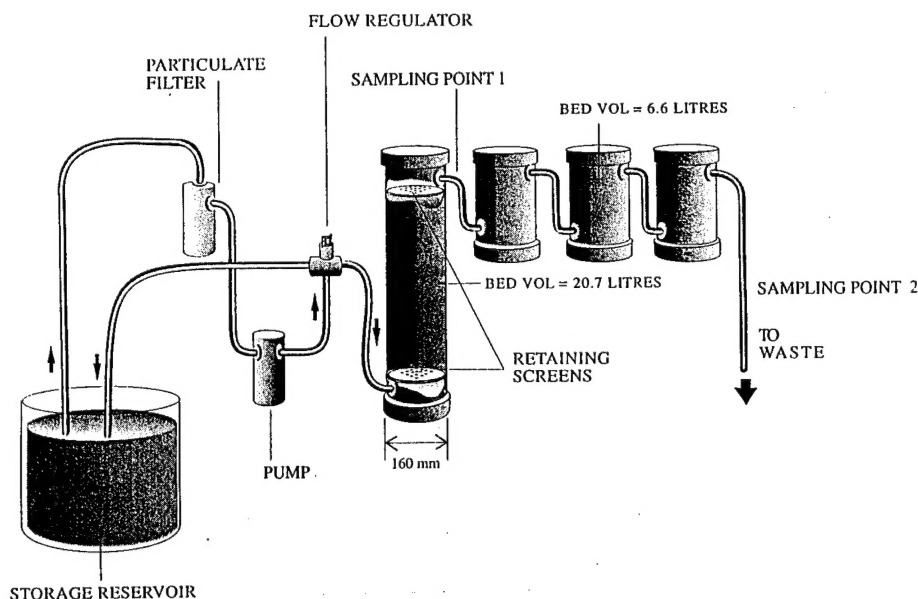


Figure 2: Schematic Diagram of Prototype #2

## 2.5 Analytical Methods

The oil and grease concentrations in test OWWs were determined using Standard Method 5520 C Partition Infra-red (APHA, 1989), modified by substituting methylene chloride for trichlorotrifluoroethane in the extraction process. The percentage of extractable oil and grease in detergents was measured by accurately weighing 100 mg of a detergent and dissolving it in 1 litre of deionised water and analysing by Standard Method 5520 C. Dead volumes were determined by adding an inorganic substance (copper sulfate and sodium hydroxide) that could be identified in the effluent.

## 3. Results and Discussion

### 3.1 Effect of Test OWW Composition on Effluent Quality

A polishing unit used after traditional plate or centrifugal separators will have to treat an influent waste stream which consists of emulsified oils, detergents and mixtures of seawater and fresh water. No free oil would be expected. A test OWW was prepared to simulate these conditions. The detergents tested are used on RAN ships and cover a range of properties. Gamosol is a nonionic strongly emulsifying detergent commonly used in RAN engine and machinery spaces. It contains alkylethoxylate surfactants and 720 g/l of aromatic and aliphatic petroleum distillate (Gamlen, 1991) and has 87% w/w extractable oil and grease. Comprox is a general purpose anionic cleaner that contains 33% linear alkylbenzene sulfonate, coconut diethanolamide and alkylethoxylates (Premoselli, 1988). It has only 8% w/w extractable oil and grease. Vecom is a fast breaking detergent which the RAN is currently seeking to use instead of Gamosol. It contains 2.5% of a di-fatty acid terminated polyethylene glycol ester and the remainder of the organic component is petroleum distillate (Vecom, 1991). It contains 79 % w/w extractable oil and grease.

Table 1 lists the results obtained for the effluent using Prototype # 1 with a variety of test OWWs and a flow rate of 2.3 l/min. The unit failed to produce an effluent which met the <15 mg/l limit when Gamosol or high oil concentrations were present.

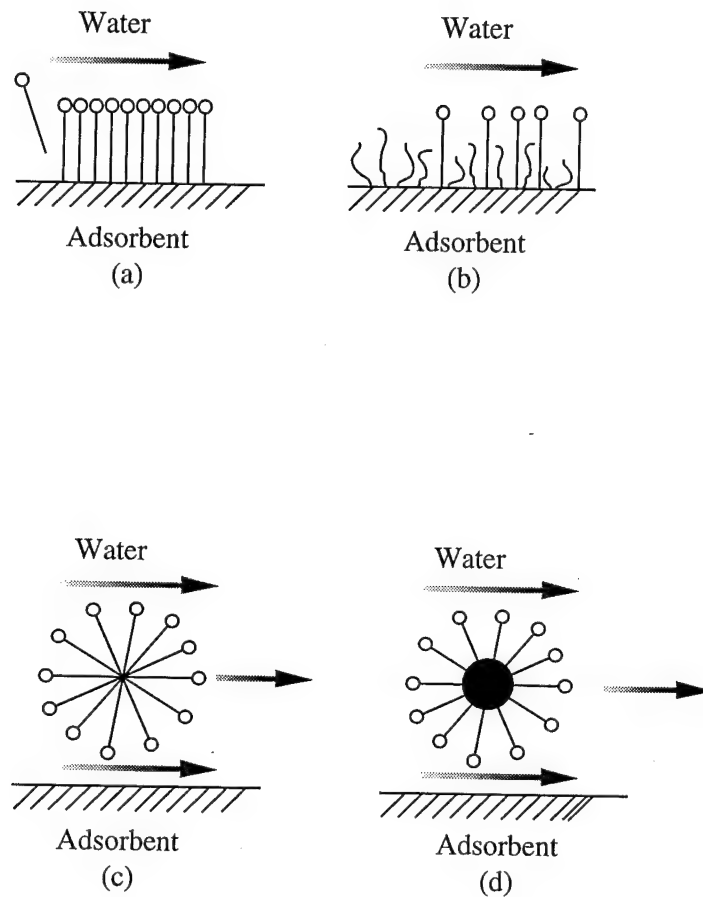
The presence of some detergents in the test OWW had a large effect on adsorbent performance. The strongest emulsifying detergent, Gamosol, consistently reduced the oil adsorption efficiency. When Vecom and Gamosol were both added the final concentration of oil and grease in the effluent exceeded the initial contribution expected from the oil mix. It appears that the petroleum spirit present in Vecom and Gamosol also failed to be effectively adsorbed in the presence of Gamosol. Both Comprox and Vecom when used alone were capable of maintaining effluent quality below the 15 mg/l guidelines.

*Table 1: Performenace of the Environ-smart Oil Filter Prototype #1 with a Variety of Test Oily-Water Wastes*

| OWW Content<br>(Nominal Concentrations)<br>(mg/l) | Initial Oil/Grease<br>Concentration<br>(mg/l) | Final Oil/Grease<br>Concentration<br>(mg/l) | % Removal |
|---|---|---|-----------|
| 100 oil mix                                       | 85  | 3   | 96        |
| 100 oil mix and 100 Vecom                         | 266   | 4   | 98        |
| 100 oil mix and 100 Comprox                       | 69  | 8   | 88        |
| 100 oil mix and 100 Gamosol                       | 165   | 68  | 59        |
| 100 oil mix, 100 Vecom and 100 Gamosol            | 274   | 155   | 43        |
| 1000 oil mix                                      | 1100  | 29  | 97        |

Surfactant molecules can behave in two distinct ways depending on their concentration relative to their critical micelle concentration (CMC). Below the CMC, surfactant molecules will exist as individual molecules and the presence of the hydrophobic group will interfere with the hydrogen bonding of water molecules which will encourage surfactant molecules to leave the bulk fluid and adsorb at surfaces. When a hydrophobic adsorbent is present, surfactant molecules will align and be adsorbed (Figure 3). At concentrations above the CMC, surfactant molecules will aggregate forming micelles (Figure 3). These will be thermodynamically more stable in the fluid phase because the hydrophilic group is at the outer surface of the micelle. Consequently, micelles will be less likely to adsorb to hydrophobic adsorbents (Chatterjee, 1985). Surfactant micelles will also contain entrained oil which may also reduce adsorbency by blocking the contact of the oil with the hydrophobic adsorbent (Figure 3).

Fast breaking detergents such as Vecom are specifically designed to have a high CMC. In addition, Vecom has two hydrophilic functional groups which will sterically interfere with micelle formation. Consequently, at a concentration of 100 mg/l it was expected that Vecom would not form micelles and is best represented by Figure 3a. Gamosol on the other hand is intended to emulsify oils and greases during wash down of tanks and to disperse floating oils. To achieve this a stable emulsion is required. The surfactant in Gamosol is an alkylethoxylate which has a large hydrophobic chain which reduces alkylethoxylate's CMC. Consequently, Gamosol has a low CMC and at 100 mg/l, the bulk of the surfactant was expected to be present as micelles and can be best represented by Figure 3c. Comprox consists mostly of an anionic surfactant and these generally have CMCs which are 3 or 4 orders of magnitude higher than straight chain nonionic surfactants, such as Gamosol (Chatterjee, 1985). However, Comprox also contains some alkylethoxylates and consequently the surfactants from this detergent may be present both as dissolved surfactant (Figure 3a) and as micelles (Figure 3c).



**Figure 3: Schematic Model of Surfactant Behaviour Below and Above the CMC.**

Where (a) shows alignment of surfactant molecules below the CMC preferentially on the hydrophobic adsorbent surface with hydrophilic groups in contact with water; (b) models the adsorption of oil and detergent below the CMC on the hydrophobic surface, oil and grease molecules do not form ordered arrangements and can form multiple layers; (c) shows the behaviour of surfactants above the CMC, where they form a stable arrangement in the water phase, with a surface of hydrophilic functional groups that do not readily adsorb onto hydrophobic surfaces; (d) shows the behaviour of surfactants and oils above the detergents CMC, where entrained oil molecules are isolated from the hydrophobic surface.

The above rationale is consistent with the observations in Table 1 where the presence of Vecom which has a high CMC and was expected to be adsorbed, had no observable effect on effluent quality, Comprox interfered slightly, and Gamosol which has been particularly formulated to form stable micelles and has a low CMC, substantially interfered with the adsorption process.

When a 1000 mg/l oil mix was used instead of 100 mg/l (Table 1), the effluent quality exceeded the regulatory limit. However, the percentage removal was similar to the lower concentration oil mix and when fast break detergent was present. Very limited data is available on the effect of oil concentration on adsorbance. However, adsorption at higher oil concentrations could be improved by increasing the adsorbent volume. However, it is unlikely that when installed onboard as a polishing unit this system would face an influent with such a high oil and grease concentration.

### 3.2 Effect of Flowrate on Effluent Quality

The space available on RAN ships is extremely limited and consequently, any additional OWW separating equipment should be compact. For this reason any adsorption unit installed would ideally be able to handle high flowrates. For example, a DDG class produces approximately 24 tonne/day of OWW (Jabs, pers comm, 1995) and treating that volume in any hydrocarbon filter would require a flowrate of 16.7 l/min. Table 2 lists the results of tests done at a higher flowrate of 5.4 l/min.

Table 2: Performance of Environ-smart Oil Filter Prototype #1 at a Flowrate of 5.4 l/min

| OWW Content<br>(Nominal Concentrations)<br>(mg/l) | Initial Oil/Grease<br>Concentration<br>(mg/l) | Final Oil/Grease<br>Concentration<br>(mg/l) | % Removal |
|---|---|---|-----------|
| 100 oil mix                                       | 68  | ~5  | 93        |
| 100 oil mix                                       | 60  | 1   | 98        |
| 100 oil mix and 100 Vecom                         | 188   | ~5  | 97        |
| 100 oil mix and 100 Comprox                       | 87  | 15  | 83        |
| 100 oil mix and 100 Gamosol                       | 147   | 109   | 26        |

When only oils and Vecom were present, adsorption efficiency was unaffected by increasing flowrates. However, when Comprox and Gamosol were present, an effect was observable. The adsorption efficiency when Comprox was present, was only marginally lower at this higher flowrate, however, the MARPOL limit was reached. The presence of Gamosol had a substantial effect with the adsorption efficiency dropping from 59% to 26%.

Reduced adsorption at higher flowrates can be attributed to a number of factors. Increasing the flowrate will result in a shorter contact time which could be significant if adsorption kinetics are slow. Alternatively, a physical effect of increased velocity through the adsorbent bed could interfere with the adsorption process.

Adsorption of hydrophobic oils and greases will be mainly due to dispersive (van der Waals) forces, and contributions from polar attraction and hydrogen bonding will be minimal. Dispersion is the least energetic attractive force and is reversible. The kinetics of physical adsorption are generally rapid because no electron transfer or chemical bonding is necessary. Physical adsorption which relies on dispersive forces is readily reversible, however, generally equilibrium partitioning of the sorbate, in this case oil and grease, in the water and the adsorbed phases will dictate the overall adsorption performance (Ruthven, 1991).

One possible reason for the large effect of flowrate on adsorbent performance may be associated with the design of the unit. The free volume of prototype #1 was found to be only 11 litres, well below the expected volume. Total system volume was greater than 40 litres with 20 kilos of adsorbent. Therefore, a void volume of greater than 20 litres was expected. Consequently, some short cutting of the adsorbent bed must have occurred. The most likely explanation is that the design of this prototype (Figure 1) results in much of the adsorbent bed lying under the level of the outlets, and accordingly it may not have been in proper contact with the OWW. Another possible explanation is that channelling may have occurred which allowed some influent to proceed through the system without properly contacting the adsorbent.

### 3.3 Effect of Adsorbent Unit Design

An additional housing for the adsorbent was made which had no adsorbent below the outlet, and which contained similar adsorbent mass. The free volume of prototype #2 was found to be 34 litres. Table 3 lists the results with this unit.

*Table 3: Performance of Oil Filter Prototype #2.*

| OWW Content<br>(Nominal concentration)<br>(mg/l) | Flowrate<br>(l/min) | Set-up | Initial<br>oil/grease<br>(mg/l) | Intermediate<br>Sampling Point<br>oil/grease<br>(mg/l) | Final<br>oil/grease<br>(mg/l) | %<br>Final<br>Removal |
|--|---------------------|--------|---------------------------------|--|-------------------------------|-----------------------|
| 100 oil mix                                      | 10.4                | #1     | 103                             | 12   | 7                             | 93                    |
| 100 oil mix                                      | 2.5                 | #1     | 96                              | 9  | 7                             | 93                    |
| 100 oil mix                                      | 2.5                 | #2     | 88                              | 9  | 8                             | 91                    |
| 100 oil mix and 100 Vecom                        | 2.5                 | #2     | 142                             | 15   | 7                             | 95                    |
| 100 oil mix and 100 Comprox                      | 2.5                 | #2     | 80                              | 53   | 32                            | 60                    |
| 100 oil mix and 100 Gamosol                      | 2.5                 | #2     | 157                             | 132  | 106                           | 32                    |
| 1000 oil mix                                     | 2.5                 | #2     | 790                             | 101  | 36                            | 95                    |

When oil mix or oil mix with Vecom were present this unit had an adsorption removal efficiency similar to prototype #1. Also, flowrate and direction of flow had no observable effect on the effluent quality. However, when Comprox and Gamosol were present this prototype performed worse than the previous unit (Table 1 and Table 2). The major difference between the two designs was the velocity of the influent through the adsorbent bed caused by the smaller diameter housing.

Comparing the results for samples taken at the two different sampling points (Table 3), it is observed that oil removal efficiency was dependent on the volume or mass of the adsorbent bed when strongly emulsifying detergents, such as Gamosol, were present. Above the CMC, Gamosol surfactants will be present as a mixture of free soluble surfactants and micelles. While Gamosol has a low CMC and was expected to be present mainly as micelles, some free surfactant would also have been present. This free surfactant would have adsorbed and caused a redistribution of surfactants until a new equilibrium was established. Consequently, as the solution proceeded through the adsorbent bed new equilibrium concentrations of micelles and free surfactant would have formed. By this process oils and surfactants would eventually have been adsorbed. This process is much slower than straight adsorption of free surfactant and requires much longer contact times and adsorbent bed length. More adsorbent will therefore be required to adsorb the same amount of oils in the presence of some detergents. Consequently, effluent quality can be improved by increasing the unit size.

However, in the absence of strongly emulsifying detergents an adsorbent bed volume of approximately 40 litres can produce the desired effluent quality. Moreover, in the absence of such detergents, the oil and grease concentration in the effluents coming from current plate and centrifugal separators should be lower. This would reduce the demand on any polishing unit. At the maximum flowrate of 10.4 l/min, oil adsorption was unaffected. Consequently, a compact unit could be designed to polish shipboard OWW if shipboard use of strongly emulsifying detergents is avoided.

Contact time cannot entirely explain the difference in observed effluent quality because the contact time in prototype #2 which performed worst (13.6 minutes) was much greater than the calculated contact time in prototype #1 (4.7 -2.0 minutes). The speed of the OWW through the adsorbent bed must also have been affecting effluent quality. At higher hydraulic velocity, detergent solutions can dislodge adsorbed oils and grease molecules from solid surfaces more readily and re-emulsify them (Rosen, 1988). Surfactants do this by reducing the amount of work required to dislodge adsorbed oils and other substances (Rosen, 1988). This depends on molecular surfactant being present next to the adsorbed layer. Accordingly, at faster hydraulic velocity surfactant replacement will be quicker and more energy will be available to dislodge adsorbed oils and surfactants (Rosen, 1988). Therefore, when surfactants above their CMC are present there will be competing mechanisms where the slowly adsorbing hydrocarbon and surfactant molecules will also be re-emulsified at high hydraulic velocities.



For detergents below their CMC, some dislodgment of adsorbed oils could also be occurring. However, the redissolved oils and greases will be readily re-adsorbed by the adsorbent because no micelles are present to stabilise oil in the water phase.

Hydraulic currents or velocity through the adsorbent bed will have an effect on performance, especially in the presence of emulsifying detergents. Consequently, housings for hydrocarbon adsorbents should be designed to reduce hydraulic velocities if detergents may be present. This could be achieved by having larger diameter housings.

## 4. Conclusion

Oil adsorbents can polish effluents from plate and centrifugal separators provided two conditions are met. Firstly, strongly emulsifying detergents like Gamosol interfere and their use should be discontinued. Discontinuing their use will also help improve the separation efficiency of current separators, putting less demand on add-on polishing adsorbents. Secondly, care must be exercised in designing the housing for the oil adsorbent to maximise flowrates while minimising internal velocity and turbulence. This could be achieved by having a unit with a large diameter relative to its height.

## 5. Acknowledgements

The authors wish to thank Mr. G. Mathys and Mr. B. Turner for the IR analysis of oil and grease concentrations and Mr. Noel Spooner from Environ-smart for providing the oil adsorbent and test units.

## 6. References

- Anon, (1995). Separators have to perform tasks for which they were not designed. *Marine Engineers Review*, March, p. 15-19.
- APHA (1989). *Standard Methods For The Examination of Water and Wastewater*, 17th Ed. APHA, AWWA and WPCF, Washington
- Chatterjee, P. K. (1985). *Absorbency*. Elsevier, Amsterdam.
- Doerffer, J. W. (1992). *Oil Spill Response in the Marine Environment*. Pergamon Press, Oxford.

Gamlen, (1987). *Gamosol D5 Product Safety Data Sheet*. Gamlen (Australasia) Pty Ltd, Lane Cove, NSW.

Guida, R. A. (1994). Environmental compliance in the Navy. *Naval Engineers Journal*. September, p. 60-67.

Haupt, E. (1989). Bilge water oil separator system for German Navy vessels. *Naval Engineers Journal*, March, p. 44-47.

Hodgeman, D. K. C., Upsher, F. J. & Fletcher, L. E. (1995) *Hydrogen sulfide Generation in Shipboard Oily-water Wastes Part 1: Origin of Hydrogen Sulfide*. Defence Science and Technology Organisation, DSTO-TR-0053.

IMO (1992). *MARPOL 73/78 Consolidated Edition, 1991*. International Maritime Organisation, London

Jabs, V. (1995). Personal Communication. Project 1160, Royal Australian Navy, Director Naval Engineering Requirements - Ship Structures.

Premoscelli, M. (1988). Personal Communication. BP Australia Ltd., Melbourne.

Rosen, M. J. (1988). *Surfactants and Interfacial Phenomena*. John Wiley & Sons, New York.

Ruthven, D. M. (1991). Adsorption. *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th Ed. John Wiley & Sons, New York.

Smookler, A. & Alig, C. (1992). The Navy's shipboard waste management research and development program. *Naval Engineers Journal*, May, p. 89-97.

Vecom, (1991). *Product Information*. Port Marine Services Pty Ltd, Port Melbourne, Vic.

|   |  |                               |   |  |  |
|---|--|-------------------------------|---|--|--|
| <b>DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION</b><br><br><b>DOCUMENT CONTROL DATA</b>  |  |                               |   | 1. PAGE CLASSIFICATION<br><b>UNCLASSIFIED</b>                              |  |
|   |  |                               |   | 2. PRIVACY MARKING/CAVEAT (OF DOCUMENT)                                    |  |
| 3. TITLE<br><br>Hydrocarbon adsorbents: a potential polishing step to treat shipboard oily-water waste  |  |                               | 4. SECURITY CLASSIFICATION (FOR UNCLASSIFIED REPORTS THAT ARE LIMITED RELEASE USE (L) NEXT TO DOCUMENT CLASSIFICATION)<br><br>Document (U)<br>Title (U)<br>Abstract (U) |  |  |
| 5. AUTHOR(S)<br><br>Lyn E. Fletcher and F. J. Upsher  |  |                               | 6. CORPORATE AUTHOR<br><br>Aeronautical and Maritime Research Laboratory<br>PO Box 4331<br>Melbourne Vic 3001   |  |  |
| 7a. DSTO NUMBER<br>DSTO-TR-0237   |  | 7b. AR NUMBER<br>AR 009-374   |   | 7c. TYPE OF REPORT<br>Technical Report                                     |  |
| 8. DOCUMENT DATE<br>January 1996  |  |                               |   |  |  |
| 9. FILE NUMBER<br>510/207/0489  |  | 10. TASK NUMBER<br>NAV 94/071 |   | 11. TASK SPONSOR<br>DNER-SS  |  |
|   |  |                               |   | 12. NO. OF PAGES<br>11   |  |
|   |  |                               |   | 13. NO. OF REFERENCES<br>15  |  |
| 14. DOWNGRADING/DELIMITING INSTRUCTIONS   |  |                               |   | 15. RELEASE AUTHORITY<br><br>Chief, Ship Structures and Materials Division |  |
| 16. SECONDARY RELEASE STATEMENT OF THIS DOCUMENT<br><br>Approved for public release<br><br>OVERSEAS ENQUIRIES OUTSIDE STATED LIMITATIONS SHOULD BE REFERRED THROUGH DOCUMENT EXCHANGE CENTRE, DIS NETWORK OFFICE, DEPT OF DEFENCE, CAMPBELL PARK OFFICES, CANBERRA ACT 2600   |  |                               |   |  |  |
| 17. DELIBERATE ANNOUNCEMENT<br><br>Announcement of this report is unlimited   |  |                               |   |  |  |
| 18. CASUAL ANNOUNCEMENT YES   |  |                               |   |  |  |
| 19. DEFTTEST DESCRIPTORS<br><br>Hydrocarbon Adsorbents; Waste water; Ocean environments; Oily water waste; detergents; Contaminants; Oil pollution;   |  |                               |   |  |  |
| 20. ABSTRACT<br><br>Current shipboard oily-water waste (OWW) separators installed on RAN ships frequently fail to reduce oil concentrations in OWW to specified discharge limits. The presence of detergents is the major interference. This report examines the potential of hydrocarbon adsorbents to polish OWW containing detergents, to meet the 15 mg/l MARPOL discharge limit. Test OWWs were prepared containing a variety of detergents and tested with a hydrocarbon adsorbent. Results showed that strongly emulsifying detergents affected effluent quality, although some oil reduction in the effluent was experienced. Other less strongly emulsifying detergents, particularly fast breaking detergents, had little effect on oil and grease concentrations in the effluent. When these detergents were present in OWW, oil and grease concentrations could be reduced to less than 15 mg/l. Flow rates and adsorbent housing design also affected effluent quality when strongly emulsifying detergents were present. Consequently, hydrocarbon adsorbents could be used to reduce oil concentrations to the lower MARPOL discharge limit of 15 mg/l, provided some restrictions are also placed on shipboard detergent use, and adsorbent housings are constructed to minimise internal turbulence. |  |                               |   |  |  |

Hydrocarbon adsorbents: a potential polishing step to treat shipboard oily-water waste

Lyn E. Fletcher and F. John Upsher

**AUSTRALIA**

**TASK SPONSOR: DNER-SS**

**DEFENCE ORGANISATION**

**Defence Science and Technology Organisation**

Chief Defence Scientist  
FAS Science Policy  
AS Science Corporate Management  
Counsellor Defence Science, London (Doc Data Sheet only)  
Counsellor Defence Science, Washington  
Scientific Adviser to Thailand MRD (Doc Data Sheet Only)  
Scientific Adviser to the DRC (Kuala Lumpur) (Doc Data Sheet Only)  
Senior Defence Scientific Adviser/Scientific Adviser Policy and Command  
(shared copy)  
Navy Scientific Adviser  
Scientific Adviser - Army (Doc Data Sheet and distribution list only)  
Air Force Scientific Adviser  
Director Trials  
DME  
DCPS

} shared copy

**Aeronautical and Maritime Research Laboratory**

Director AMRL  
Chief, Ship Structures and Materials Division  
Dr D.B. Paul  
F.J. Upsher  
Lyn E. Fletcher

**DSTO Library**

Library Fishermens Bend  
Library Maribyrnong  
Library DSTOS ( 2 copies)  
Library, MOD, Pyrmont (Doc Data sheet)

**Defence Central**

OIC TRS, Defence Central Library  
Officer in Charge, Document Exchange Centre (DEC), 11 copies  
Defence Intelligence Organisation  
Library, Defence Signals Directorate (Doc Data Sheet only)

**Army**

Director General Force Development (Land), (Doc Data Sheet)  
ABCA Office, G-1-34, Russell Offices, Canberra (4 copies)  
SO (Science), HQ 1 Division, Milpo, Enoggera, Qld 4057

## Navy

Director General Force Development (Sea)  
SO (Science), Director of Naval Warfare, Maritime Headquarters Annex,  
Garden Island, NSW 2000. (Doc Data Sheet only)

## UNIVERSITIES AND COLLEGES

Australian Defence Force Academy  
Library  
Head of Aerospace and Mechanical Engineering  
Deakin University, Serials Section (M list)), Deakin University Library,  
Geelong, 3217  
Senior Librarian, Hargrave Library, Monash University

## OTHER ORGANISATIONS

NASA (Canberra)  
AGPS

## ABSTRACTING AND INFORMATION ORGANISATIONS (Public Release only)

INSPEC: Acquisitions Section Institution of Electrical Engineers  
Library, Chemical Abstracts Reference Service  
Engineering Societies Library, US  
American Society for Metals  
Documents Librarian, The Center for Research Libraries, US

## INFORMATION EXCHANGE AGREEMENT PARTNERS (PUBLIC RELEASE ONLY)

Acquisitions Unit, Science Reference and Information Service, UK  
Library - Exchange Desk, National Institute of Standards and  
Technology, US